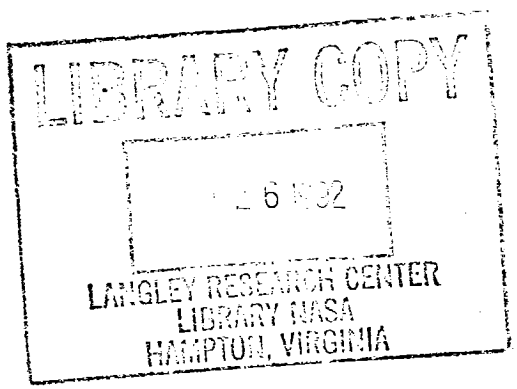
# NASA Technical Memorandum 104198

NASA-TM-104198 19920010793

# Polyimides with Pendent Ethynyl Groups

Brian J. Jensen
Paul M. Hergenrother
Godson Nwokogu




January 1992

National Aeronautics and
Space Adminstration

**Langley Research Center**
Hampton, Virginia 23665-5225

# Polyimides With Pendent Ethynyl Groups

by

Brian J. Jensen and Paul M. Hergenrother
NASA Langley Research Center
Hampton, VA 23665-5225

and

Godson Nwokogu
Hampton University, Hampton, VA 23668

## Introduction

Polyimides have received a significant amount of attention over the last thirty years and many polyimides are now commercially available in the form of adhesives, coatings, composite matrices, films, fibers, foams, membranes and moldings. Polyimides offer an attractive combination of high thermal stability and high mechanical properties . The market for polyimides in 1988 was estimated to be ~$550 M.[1] A recent book summarizes the chemistry, properties and uses for polyimides.[2]

As part of the work on polyimides, ethynyl (acetylenic) groups have been placed on the ends of imide oligomers[3,4] and pendent along the polymer backbone.[5] A series of acetylene terminated imide oligomers designated Thermid™ are available from National Starch and Chemical Corp., Bridgewater, NJ. A review of acetylene containing prepolymers was published.[6] The work reported herein concerns the use of novel ethynyl containing diamines to prepare a series of polyimides containing pendent ethynyl groups. The unsubstituted diamine, often referred to as 3F diamine, and polyimides therefrom were previously reported.[7] Our work was done as part of a study on chemical structure/property relationships to provide

information to help design better materials for a variety of aerospace applications.

## Experimental

Monomers- The monomers containing pendent ethynyl and substituted ethynyl groups were synthesized as shown in Eqs. 1 and 2. 4-Bromotrifluoro-acetophenone was prepared by reacting 1-bromo-4-lithiobenzene with ethyl trifluoroacetate at -78°C followed by warming to room temperature (RT) during about 12h. After work-up, the resulting yellow liquid was purified by vacuum distillation to obtain the desired product in 88% yield. Reaction of 4-bromo-trifluoroacetophenone with aniline hydrochloride in refluxing aniline provided 1,1-bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane in 77% crude yield. Recrystallization from benzene provided pure product, m.p. 194-196°C. The corresponding iodo compound was synthesized in a similiar procedure starting with 1-iodo-4-lithiobenzene to provide 1,1-bis(4-aminophenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane, m.p. 171-172°C.

As shown in Eq. 2, these diamines were used to prepare the ethynyl containing materials by the palladium catalyzed displacement of the halogen with the appropriate ethynyl compound. 1,1-Bis(4-aminophenyl)-1-(4-ethynyl-phenyl)-2,2,2-trifluoroethane (EDA) was synthesized by displacing the bromo group using trimethylsilylacetylene at 80°C, followed by cleavage of the trimethylsilyl group using sodium carbonate. Purification by column chromatography with silica gel provided the monomer as a yellow powder in 78% yield, visually sintered ~ 130°C and softened ~135°C with major melting at 158°C. Anal. Calc'd. for $C_{22}H_{17}F_3N_2$: C, 72.12%; H, 4.68%; N, 7.56%. Found: C, 72.34%; H, 4.79%; N, 7.45%. 1,1-Bis(4-aminophenyl)-1-(4-hexynyl-

phenyl)-2,2,2-trifluoroethane (HDA) was synthesized by displacing the bromo group with 1-hexyne under the same reaction conditions. Purification by column chromatography with silica gel provided the monomer in 76% yield, visually sintered at 137°C and softened at 144°C with major melting at 148°C. Anal. Calc'd. for $C_{26}H_{25}F_3N_2$: C, 73.92%; H, 5.96%; N, 6.63%. Found: C, 74.29%; H, 6.13%; N, 6.63%. 1,1-Bis(4-aminophenyl)-1-(4-phenylethynyl-phenyl)-2,2,2-trifluoroethane (PEDA) was synthesized by displacing the iodo group with phenylacetylene under similiar conditions. Purification by column chromatography with silica gel provided the monomer as a yellow powder in 58% yield, visually sintered at 85°C and softened at 90-92°C with major melting at 98°C. Anal. Calc'd. for $C_{28}H_{21}F_3N_2$: C, 76.00%,H, 4.78%; N, 6.33%. Found; C, 75.63%; H, 4.95%; N, 6.15%. The other monomers used in this study, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), and 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (BDAF) were obtained from commercial sources and were sublimed or recrystallized prior to use.

Polymers- The polyamide acids were prepared by adding the dianhydride to a solution of the diamine in N,N-dimethylacetamide (DMAc) followed by stirring for ~16h at RT under nitrogen (Eq. 2). The polyamide acids were either thermally imidized (1h each at 100, 200, 300°C) or chemically imidized by adding acetic anhydride and triethylamine to the polyamide acid solution and stirring overnight. Copolymers were prepared under the same reaction conditions using 10 mole % of the ethynyl containing diamine and 90 mole % of BDAF.

Characterization- Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Inherent viscosities ($\eta_{inh}$) were obtained on 0.5% solutions in DMAc at 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent Tg taken at the inflection point of the $\Delta T$ versus temperature curve. Thermogravimetric analysis (TGA) was conducted on film specimens at a heating rate of 2.5°C/min in flowing air or nitrogen.

Films- DMAc solutions (15% solids) of the polymers and copolymers were centrifuged, the decantate doctored onto plate glass and dried at RT to a tack-free form in a low humidity chamber. The films on glass were dried 1h each at 100, 200, and 300°C in air. Mechanical tests were preformed according to ASTM D882 on four or more specimens per test condition.

## Results and Discussion

The ethynyl and substituted ethynyl diamines were prepared in relatively high crude yields but purification by simple recrystallization was difficult. Column chromatography proved more successful and afforded diamines whose elemental analyses agreed well with the theoretical values. The ethynyl diamines visually melted over a broad range and sintered and softened prior to melting, indicative of impure material. However, by DSC at a heating rate of 20°C/min, EDA and HDA exhibited relatively sharp melting endotherms at 176 and 141°C, respectively. PEDA exhibited a broad endotherm peaking at 76°C. The exothermic peaks in the DSC curves due to reaction of the ethynyl groups occurred at 261°C for EDA, 300°C for HDA and 370°C for PEDA showing that the substituent on the ethynyl group influenced the curing reaction. The chemical structure and purity of all of the ethynyl

containing diamines were further verified by mass spectroscopy and $^1H$ NMR. The detailed synthesis and characterization of the precursor compounds and the ethynyl containing diamines will be published elsewhere.

Low inherent viscosities and presumably low molecular weights were obtained for the polyamide acids from the reaction of HDA with BTDA or 6FDA as shown in Table 1. This has been tentatively attributed to the purity of HDA even though the DSC melting endotherm, elemental analysis and $^1H$ NMR suggested relatively high purity. High inherent viscosities were obtained for polyamide acids from the reaction of EDA and PEDA with BTDA and 6FDA. As a reminder, the DSC melting endotherm of PEDA was broad and not characteristic of a high purity material. When the polyamide acid solutions were cast as thin films on plate glass and subsequently dried in air through 1h at 300 °C (350°C for the PEDA polymers only), no Tgs by DSC could be detected and the films were very brittle as expected because of the high crosslink density. No further work was done with these polymers because of their limited utility.

The focus shifted to the preparation of copolymers that would yield more useable materials with a lower crosslink density. Copolymers were prepared from the reaction of 90 mole % of BDAF and 10 mole % of the ethynyl diamines with 6FDA. The properties of the copolymers are presented in Tables 2 and 3. Inherent viscosities of the polyamide acids and corresponding polyimides were high. The polyamide acids were chemically converted to the polyimides which were readily soluble in chloroform and DMAc. The polyimides exhibited the same initial Tgs as expected since the difference in chemical structure is minor (the pendent ethynyl group substituent) and all the polyimides were high molecular weight as suggested by the inherent viscosities.

The temperature of 5% weight loss by TGA and RT thin film properties are presented in Table 3. The HDA derived polymer exhibited the poorest thermal stability by TGA in air with 5% weight loss occurring at 401°C. In nitrogen, the temperature of 5% weight loss was the same for the three copolymers. Thin films of the copolymers dried for 1h at 300°C (350°C, PEDA polymer only) in air exhibited RT tensile strengths and moduli of 14.8-17.8 ksi and 416-534 ksi, respectively. The RT modulus of the uncrosslinked BDAF/6FDA polyimide was 433 ksi. All the films of the copolymers after heating for 1h at 300°C (350°C, PEDA polymer only) were insoluble but swelled in chloroform and DMAc.

## Conclusions

Diamines containing pendent ethynyl and substituted ethynyl groups were prepared and purified. Polymers and copolymers prepared from these diamines and commercially obtained dianhydrides form films which could be crosslinked thermally to improve solvent resistance. The toughness and solubility could be systematically controlled by varing the amount of ethynyl containing diamine used in the synthesis, which controls the final crosslink density.

## REFERENCES


1. J. M. Weatherall and A. T. Ono, Proc. Sym. Recent Adv. in Polyimides and Other High Perf. Polymers, Am. Chem. Soc., Div. Polym. Chem. (P. M. Hergenrother, organizer), San Diego, CA, January, 1990.

2. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, Polyimides, Blackie and Son, Ltd. Glasgow, United Kingdom, 1990. (In USA, Chapman and Hall, NY).

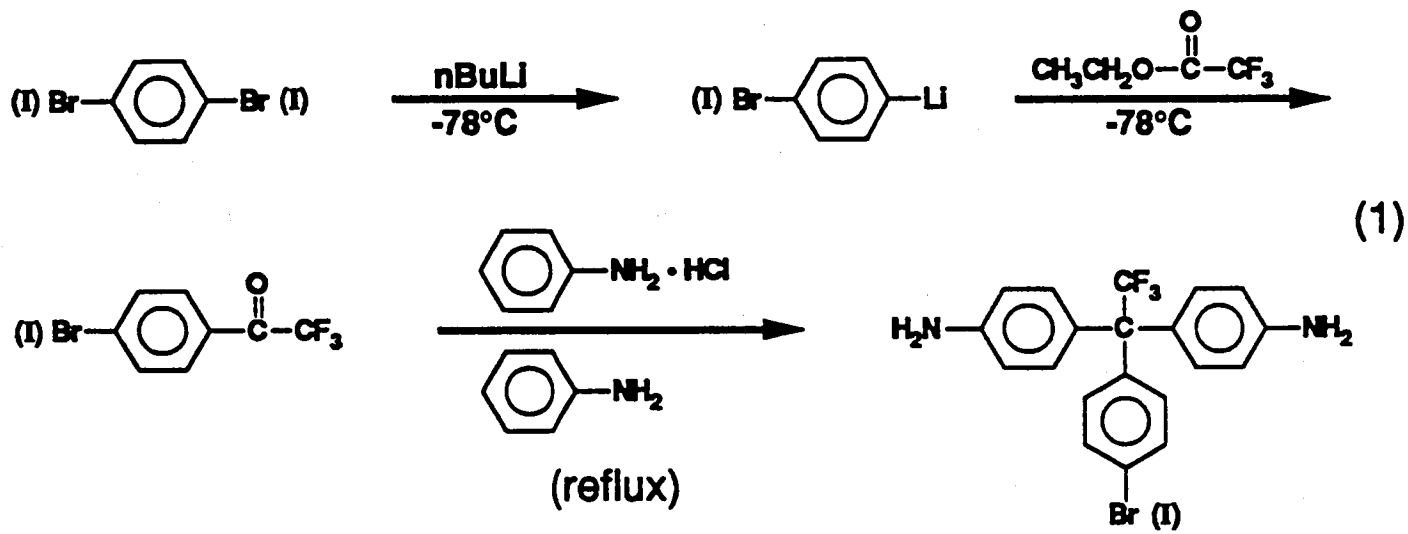
3. N. Bilow, A. L. Landis and L. J. Miller, U. S. Patent 3,845,018(1974) (To Hughes Aircraft).

4. A. L. Landis, N. Bilow, R. H. Boschan, R. E. Lawrence and T. J. Aponyi, Polym. Prepr., 15, 537(1974).

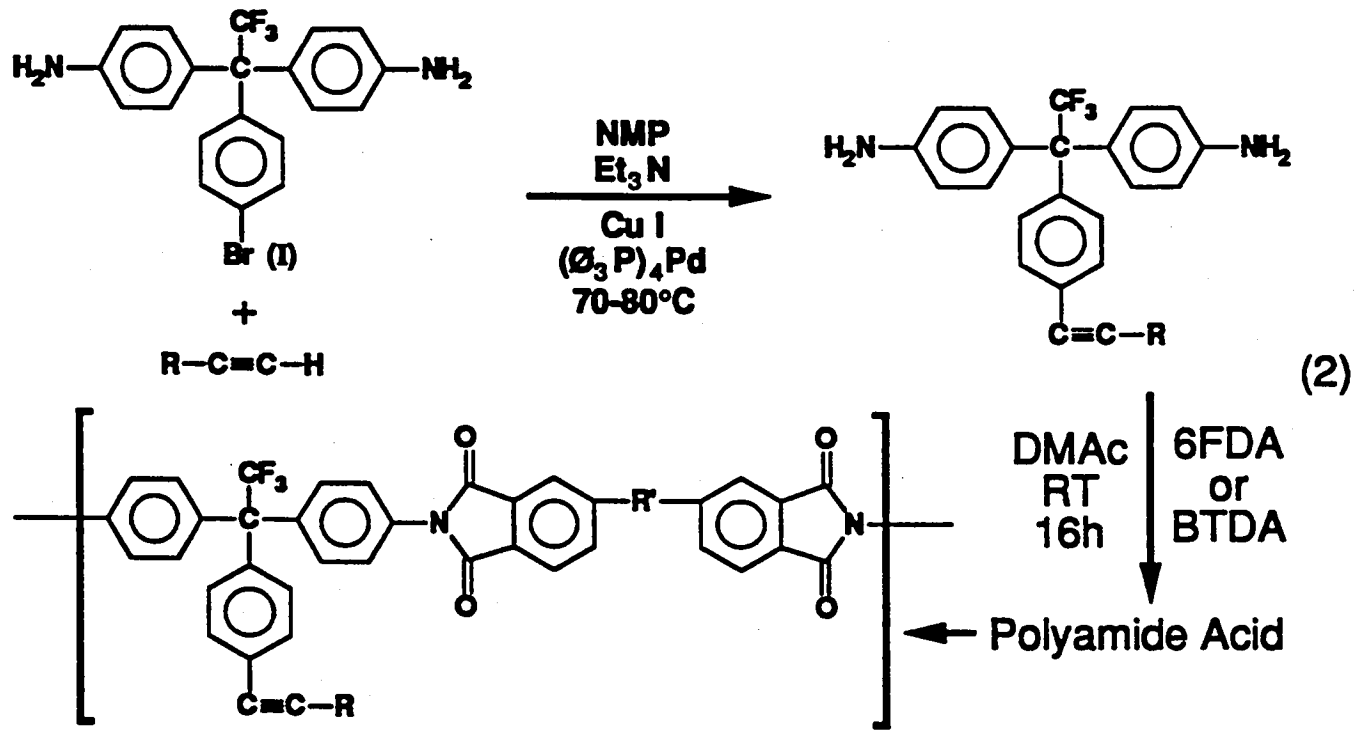
5. F. W. Harris, S. M. Podaki and S. Varaprath, Polym. Prepr., 21(1), 3(1980).

6. P. M. Hergenrother, Encyclopedia of Polymer Science and Engineering, 2nd. Ed., vol.1, John Wiley and Sons, Inc., New York, 61(1985).

7. W. B. Alston and R. F. Gratz, in Rec. Adv. in Polyimide Sci. Tech. (Edited by W. D. Weber and M. R. Gupta), Society of Plastics Engineers, Inc, Poughkeepsie, NY, 1987, p. 1.


(I) Br
Br (I)
nBuLi
-78°C
(I) Br
Li
CH3CH2O–C(=O)–CF3
-78°C
(I) Br
C(=O)–CF3
NH2 · HCl
NH2
(reflux)
H2N
CF3
C
NH2
Br (I)

(1)




In Polyimide, R = H, $C_4H_9$, $C_6H_5$

TABLE 1. INHERENT VISCOSITY OF POLYAMIDE ACIDS

| Diamine | Dianhydride | Polyamide Acid $\eta_{inh}$, dL/g |
|---|---|---|
| EDA | BTDA | 0.94 |
| EDA | 6FDA | 0.80 |
| HDA | BTDA | 0.40 |
| HDA | 6FDA | 0.26 |
| PEDA | BTDA | 0.77 |
| PEDA | 6FDA | 0.68 |

TABLE 2. CHARACTERIZATION OF 6FDA BASED COPOLYMERS

| Diamine with 90% BDAF | ηinh, dL/g | | DSC Tg, °C[a] | |
|---|---|---|---|---|
| | Polyamide acid | Polyimide[a] | Initial | Final[b] |
| 10% EDA | 1.54 | 1.34 | 265 | 275 |
| 10% HDA | 1.08 | 0.89 | 264 | 269 |
| 10% PEDA | 1.47 | 1.25 | 265 | 273 |

[a]Chemically imidized, acetic anhydride and triethylamine.

[b]After heating to 400°C.

TABLE 3. THERMAL STABILITY AND RT THIN FILM PROPERTIES OF 6FDA BASED COPOLYMERS

| Diamine Components | Temperature of 5% Wt. Loss by TGA, °C | | Tensile Strength, ksi | Tensile Modulus, ksi | Elongation, % |
|---|---|---|---|---|---|
| | Air | $N_2$ | | | |
| 10% EDA, 90% BDAF | 468 | 493 | 14.8 | 416 | 6.7 |
| 10% HDA, 90% BDAF | 401 | 493 | 17.8 | 534 | 5.9 |
| 10 % PEDA, 90% BDAF | 450 | 493 | 17.7 | 518 | 6.1 |
| 100% BDAF | --- | --- | 15.6 | 433 | 26.7 |

# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | January 1992 | Technical Memorandum |

**4. TITLE AND SUBTITLE**

Polyimides with Pendent Ethynyl Groups

**5. FUNDING NUMBERS**

505-63-50-01

**6. AUTHOR(S)**

Brian J. Jensen, Paul M. Hergenrother and Godson Nwokogu

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

NASA Langley Research Center
Hampton, VA 23665-5225

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
Washington, DC 20546-0001

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

NASA TM-104198

**11. SUPPLEMENTARY NOTES**

Use of trade names or names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration. Brian J. Jensen and Paul M. Hergenrother: NASA Langley Research Center, Hampton, VA; Godson Nwokogu: Hampton University, Hampton, VA

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

Unclassified-Unlimited
Subject Category 27

**12b. DISTRIBUTION CODE**

**13. ABSTRACT** (Maximum 200 words)

Several new polyimides containing pendent ethynyl groups have been prepared and characterized. The new polyimides were prepared from the following novel ethynyl containing diamines; 1,1-bis(p-aminophenyl)-1-(p-ethynylphenyl)-2,2,2-trifluoroethane, and 1,1-bis(p-aminophenyl)-1-(p-phenylethynylphenyl)-2,2,2-trifluoroethane, and 1,1-bis(p-aminophenyl)-1-(p-hexynylphenyl)-2,2,2-trifluoroethane by reacting with either 3,3',4,4'-benzophenone tetracarboxylic dianhydride or 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). Inherent viscosities for the polymers ranged from 0.26 to 0.94 dL/g. Three copolymers prepared by reacting 10 mole % of one of the ethynyl containing diamines and 90 mole % of 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane with 6FDA were also prepared and characterized. Inherent viscosities for these copolymers ranged from 1.08 to 1.54 dL/g. Original polyimide glass transition temperatures were ~265°C while curing at 300 to 350°C for 1 hour in air increased the Tgs by ~10°C. Film properties and thermal stability were also measured for these copolyimides.

**14. SUBJECT TERMS**

Polyimides; Ethynyl Groups, Crosslinked Polyimides

**15. NUMBER OF PAGES**

13

**16. PRICE CODE**

A03

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | | |